

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau



(43) International Publication Date
5 July 2001 (05.07.2001)

PCT

(10) International Publication Number
WO 01/47806 A1

(51) International Patent Classification⁷: **C01B 31/20** (74) Agents: RICHARDS, John; Ladas & Parry, 26 West 61st Street, New York, NY 10023 et al. (US).

(21) International Application Number: **PCT/US00/42050**

(22) International Filing Date:
10 November 2000 (10.11.2000)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
09/473,157 28 December 1999 (28.12.1999) US

(63) Related by continuation (CON) or continuation-in-part (CIP) to earlier application:
US 09/473,157 (CON)
Filed on 28 December 1999 (28.12.1999)

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(81) Designated States (national): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CR, CU, CZ, DE, DK, DM, DZ, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, TZ, UA, UG, US, UZ, VN, YU, ZA, ZW.

(84) Designated States (regional): ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).

Published:

— With international search report.

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

WO 01/47806 A1

(54) Title: PROCESS FOR SELECTIVE OXIDATION OF CARBON MONOXIDE IN A HYDROGEN CONTAINING STREAM

(57) Abstract: A process for the selective oxidation of CO to CO₂ in a hydrogen feed in the presence of catalyst containing platinum and iron. The catalyst can be acid treated.

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PROCESS FOR SELECTIVE OXIDATION OF CARBON MONOXIDE
IN A HYDROGEN CONTAINING STREAM

Field of the Invention

The invention relates to the catalytic oxidation of carbon monoxide. In another of its aspects the invention relates to the selective oxidation of carbon monoxide in the presence of hydrogen. In still another aspect the invention relates to catalyst compositions effective in the oxidation of carbon monoxide. In yet another aspect the invention relates to removing as much carbon monoxide as possible, preferably all carbon monoxide, from a stream containing carbon monoxide and hydrogen, particularly, to provide hydrogen feedstock for fuel cells.

Background of the Invention

The selective oxidation of carbon monoxide in hydrogen-rich streams has been of considerable technical interest for the purification of reformed hydrogen used in feed gas in ammonia synthesis. Recently, this selective oxidation process, sometimes referred to as preferential oxidation, has attracted interest due to the possibility of using this technology in providing suitable hydrogen fuel for fuel cells. Since carbon monoxide is also oxidized to provide carbon dioxide for carbon dioxide lasers, the use of catalyst which previously had been found useful in the oxidation of carbon monoxide for use in carbon dioxide lasers has also been investigated for adaptation for use in providing carbon monoxide-free hydrogen for fuel cell feedstock.

A fuel cell is an electrochemical device that enables converting the chemical energy of fuels directly to electricity. A hydrogen-air polymer electrolyte membrane (PEM) fuel cell stack is currently considered the best means for adapting this technology to most uses. The PEM fuel cell is most efficient using gaseous hydrogen for fuel. Use of a fuel processor to generate a hydrogen-rich feedstock at the point of use eliminates problems of storage and distribution of the hydrogen fuel.

A fuel processor can convert fuels such as alcohol, gasoline, liquid petroleum gas, or natural gas to a hydrogen-rich stream. By a process of steam reforming a stream consisting primarily of hydrogen, carbon dioxide and carbon monoxide can be produced, but the product is generally saturated with water. Processing this stream in a shift reactor reduces the carbon monoxide content to

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provide relatively more hydrogen by means of the well known water-gas-shift reaction. This reaction provides a product that contains from 0.2 to 2 percent carbon monoxide by volume which is sufficient to poison the platinum-based catalyst at the PEM anode. It has now been found that, among other possibilities for removing carbon monoxide 5 to the level necessary to prevent poisoning of the PEM catalyst, the same catalyst that is used to recombine carbon monoxide and oxygen in carbon dioxide lasers can be used to provide hydrogen feedstock for fuel cells on a level of carbon monoxide removal that is commercially viable. The operating conditions for the processes are essentially different. The removal of carbon monoxide by selective oxidation of a 10 stream containing both carbon monoxide and hydrogen can be accomplished using the same catalyst as used in carbon dioxide lasers by controlling an increased oxygen flow to the oxidation process, raising the operating temperature of the oxidation process and avoiding reaction between oxygen and hydrogen as compared to the conditions used to recombine carbon monoxide and oxygen in carbon dioxide lasers.

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Summary of the Invention

It is desirable to provide a process that is effective for catalytically oxidizing carbon monoxide with free oxygen. It is another object of this invention to provide a process for converting carbon monoxide (CO) to carbon dioxide (CO₂) in the presence of hydrogen. Again it is desirable to provide a process for producing 20 hydrogen fuel for a fuel cell in which carbon monoxide (CO) is converted to carbon dioxide (CO₂) in the presence of hydrogen on a scale that is commercially viable.

In accordance with this invention a process is provided for the selective oxidation of carbon monoxide to carbon dioxide in a gaseous mixture comprising hydrogen and carbon monoxide. In the process an amount of free oxygen is mixed 25 with the gaseous mixture comprising hydrogen and carbon monoxide to provide a second gaseous mixture having an enhanced oxygen to carbon monoxide mol ratio. The second gaseous mixture is contacted with a catalyst comprising platinum and iron impregnated on a support material. The carbon monoxide in the second gaseous mixture is thereby substantially completely converted to carbon dioxide. When used herein the terminology "substantially complete conversion of carbon monoxide to carbon dioxide" or similar terminology means that the amount of carbon monoxide

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present in a fuel cell feed stream is sufficiently low so as not to materially affect the functioning of a PEM catalyst.

Detailed Description of the Invention

According to this invention the process for oxidizing carbon monoxide
5 in a feed stream that also contains hydrogen can be carried out so that the CO is selectively oxidized in preference to the oxidation of the hydrogen thereby providing a means to deliver a highly pure hydrogen stream for fuel cell operation in which the oxidation of carbon monoxide in a hydrogen fuel can be integrated into a total package for generating a hydrogen-rich feedstock at the point of use.

10 The feed gas to the oxidation process can be formed in any suitable manner, such as by mixing the hydrogen that contains carbon monoxide contaminant with the O₂ containing air at any point before contact with the catalyst.

15 The process for oxidizing a feed containing carbon monoxide and hydrogen gas can be carried out at any pressure conditions, for any length of time, any gas hourly space velocity and any volume ratio of O₂ to CO that is suitable for selective oxidation of CO in the presence of hydrogen specified in a temperature range of about 0°C to about 300°C, preferably in a range of about 25°C to about 250°C, and most preferably in a range of about 50°C to about 200°C.

20 The pressure during the oxidation process generally is in the range of about 68.9 kPa to about 6890 kPa (about 10 psia to about 1000 psia), preferably about 96.4 kPa to about 1378 kPa (about 14 psia to about 200 psia).

The ratio of mols of O₂ in the feed gas to the mols of CO in the feed gas will generally be in the range of about 0.5 to 8.0 mol O₂/mol CO, preferably 0.5 to 4.0 mol O₂/mol CO, most preferably 0.5 to 1.5 mol O₂/mol CO.

25 The gas hourly space velocity (cc feed gas per cc catalyst per hour) can be in the range of about 100 to about 200,000, preferably from about 5,000 to about 50,000.

The hydrogen will generally be in the range of about 50-90 volume percent and the inlet CO will generally be in the range of about 0.1 to about 5 volume percent.

30 The preparation of the catalyst useful in this invention can be carried

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out by the process disclosed in USPN 5,017,357 and USPN 4,943,550, which disclose processes using the catalyst for the recombination of carbon monoxide and oxygen for carbon dioxide lasers.

Any of the well known support materials containing metal oxide can be used as support material for the composition of matter used as catalyst in the process of this invention. Presently preferred are substantially pure alumina (aluminum oxide), titania and/or magnesium aluminate spinel. More preferably, the support material can contain at least 95 weight percent Al_2O_3 or magnesium aluminate. These materials are readily available commercially.

Generally the surface area of the support material, which can be determined by the BET/ N_2 method (ASTM D3037), is in the range of about $10 \text{ m}^2/\text{g}$ to about $350 \text{ m}^2/\text{g}$. The support can be spherical, cylindrical, trilobal, quadrilobal, ring-like or irregular in shape. Spherical support material generally has a diameter in the range of from about 0.2 mm to about 20 mm, preferably from about 1 mm to about 5 mm.

The support can also be an inert porous, ceramic material in any of the shapes cited above and coated with aluminum oxide and/or magnesium aluminate spinel.

The impregnation of the support material with platinum and iron can be carried out in any suitable manner. Generally, compounds of platinum and compounds of iron are dissolved in a suitable solvent, preferably water, to prepare a solution of suitable concentration, generally containing from about 0.005 g to about 5.0 g platinum per cc of solution and about 0.005 g to about 5.0 g iron per cc of solution. Suitable compounds of both platinum and iron are nitrates, carboxylates and acetylacetones, among others, with acetylacetones currently preferred. Organic solvents, such as methanol, ethanol, acetone, ethyl acetate, toluene and the like can be used as solvents for platinum or iron according to this invention. Currently, acetone is preferred.

The support material can be soaked in a solution containing platinum compounds and/or iron compounds or can be sprayed with such a solution to impregnate the support. The ratio of impregnating solution to support material is generally such that the final composition of the catalyst contains 0.05 to about 10

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weight percent platinum, preferably about 0.1 to about 5 weight percent platinum and about 0.05 to about 20 weight percent iron, preferably from about 0.1 to about 4 weight percent iron. It is in the scope of this invention to use any weight percentage of platinum and iron at which they act as copromoters of the oxidation of CO with O₂. It 5 is presently preferred to spray a solution containing compounds of both metals onto the support, but the metal compounds can also be added separately in any order.

After impregnation the impregnated support material is heated to a temperature sufficient to drive off the solvent used in the impregnation. A flow of inert gas across the support material can be used. A temperature in the range of up to 10 about 250°C applied for about an hour is usually sufficient for the purpose.

The dried catalyst is heat treated in an oxidizing atmosphere, preferably in an atmosphere containing free oxygen (such as air) generally at a temperature ranging from about 80°C to about 700°C for a time ranging from about 0.5 hr to about 10 hours. The heat treatment is preferably done in incremental substeps. Currently, 15 the heat treatment is carried out at 150°C for 1 hour, 200°C for 2 hours and 400°C for 3 hours. Any combination of heating at a temperature for a time sufficient to calcine the impregnated support material to obtain at least one platinum oxide, optionally mixed with metallic platinum, and at least one iron oxide satisfies the requirements of this invention.

20 After the oxidation the calcined, platinum/iron impregnated support is subjected to a reduction reaction which can be carried out in any suitable manner, preferably at a temperature in the range of about 20°C to about 650°C, more preferably from about 200°C to about 500°C. Any reducing gas can be used, such as a gas containing hydrogen, CO, gaseous hydrocarbons such as methane, mixtures of the 25 above and the like. Preferably a free hydrogen containing gas, more preferably a gas stream of substantially pure hydrogen, is employed. The reducing step can be carried out for any suitable period of time from about 1 minute to about 20 hours, preferably from about 1 hour to about 5 hours.

The reduced, platinum/iron impregnated support can be further treated 30 by contact with any suitable organic or inorganic acid having a pH of less than about 7. Preferably, an aqueous solution of nitric acid or of a carboxylic acid (preferably acetic

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acid) is used. The previously reduced platinum/iron impregnated support is preferably soaked in about 0.01-16 mole/L of HNO₃ generally at a temperature of about 10°C to about 80°C for a period of about 0.01 to about 1 hour, but sufficiently to obtain incipient wetness.

5 After the acid treatment the impregnated support material is heated to a temperature sufficient to drive off the solvent used in the acid treatment. A flow of inert gas across the support material can be used. A temperature in the range of up to about 250°C applied for about an hour is usually sufficient for the purpose.

The dried, acid treated catalyst is heat treated in an oxidizing 10 atmosphere, preferably in an atmosphere containing free oxygen (such as air) generally at a temperature ranging from about 80°C to about 700°C for a time ranging from about 0.5 hr to about 10 hours. The heat treatment is preferably done in incremental substeps. Currently, the heat treatment is carried out at 150°C for 1 hour, 200°C for 2 hours and 400°C for 3 hours. Any combination of heating at a temperature for a time 15 sufficient to calcine the impregnated support material to obtain at least one platinum oxide, optionally mixed with metallic platinum, and at least one iron oxide satisfies the requirements of this invention.

Before use in the process of oxidizing carbon monoxide the oxidized, 20 acid-treated, supported platinum/iron catalyst can be activated by a reduction step that can be carried out in any suitable manner, preferably at a temperature of about 20°C to about 650°C, more preferably about 200°C to about 500°C for about 0.5 hour to about 25 20 hours, preferably about 1 hour to about 5 hours to enhance the activity of the catalyst composition for catalyzing a low temperature oxidation of CO with O₂ in the presence of hydrogen. Any reducing gas can be used: hydrogen, CO, paraffins and the like and mixtures thereof.

The following examples are presented in further illustration of the invention and are not to be construed as limiting the scope of the invention.

EXAMPLE I

A catalyst precursor was prepared by weighing about 500 grams of 1/8 30 inch alumina spheres (Alcoa S-100 activated alumina) into two medium porcelain bowls and calcined at 800°C for 16 hours in a an air-purged muffle furnace. 400

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grams of the dry, calcined alumina was placed in a large porcelain bowl and- using a conventional, plastic, hand spray bottle- was sprayed with an impregnating solution prepared by dissolving 8.07 grams of platinum (II) acetylacetone (platinum (II) 2,4 pentanedionate) and 10.13 grams of iron (III) acetylacetone in about 650 cc of acetone. The support was stirred frequently to assure an even distribution of the solution. When about 1/4 of the impregnation solution had been applied to the support the catalyst was placed in a draft oven and heated at 175°C for 45 minutes to an hour thereby driving off the acetone and partially decomposing the metal acetylacetones. The processes of spraying, stirring and heating were repeated three more times. When all the impregnating solution had been used the catalyst was divided equally into portions of about 202 grams each and placed in an air-purged muffle furnace heated at 150°C for 1 hour, 200°C for 2 hours and 400°C for 3 hours. This heat treatment provided two 202 gram portions of oxidized 1.0 weight percent platinum/ 0.4 weight percent iron on alumina as catalyst precursor.

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EXAMPLE II

A 202 gram portion of catalyst precursor was transferred to a 2 inch diameter quartz reactor which was then mounted in a vertical tube furnace. The catalyst was activated by reducing at 300°C with about 200 cc/min hydrogen gas downflow at atmospheric pressure for three hours. The catalyst and reactor were cooled under hydrogen flow followed by nitrogen purge thereby providing an activated catalyst. This is Catalyst A.

EXAMPLE III

Another 202 gram portion of the catalyst precursor was transferred to a 2 inch diameter quartz reactor and mounted in a vertical tube furnace. The catalyst was reduced at 300°C with about 200 cc/min hydrogen gas downflow at atmospheric pressure for three hours. The catalyst and reactor were cooled under hydrogen flow followed by nitrogen purge. The freshly reduced catalyst was poured into a large bowl and impregnated in a ventilated hood with about 60 cc of concentrated nitric acid. The acid impregnation was done dropwise with stirring. The impregnation was done as quickly as possible to minimize oxidation by exposure to atmospheric oxygen. The acid treated catalyst was dried and calcined in an air-purged muffle furnace heated at

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150°C for 1 hour, 200°C for 2 hours and 400°C for 3 hours. The catalyst was transferred to a 2 inch diameter quartz reactor which was then mounted in a vertical tube furnace. The catalyst was activated by reducing at 300°C with about 200 cc/min hydrogen gas downflow at atmospheric pressure for three hours. The catalyst and
5 reactor were cooled under hydrogen flow followed by nitrogen purge thereby providing an activated, acid-treated catalyst. This is catalyst B.

EXAMPLE IV

For these conversion runs the following equipment was used. There were two separate Brooks 5850E mass flow controllers- one for the CO feed blend and
10 one for airflow. The CO blend was held in a 30-liter, aluminum, high-pressure cylinder. The CO blend normally was 1.0 percent CO with the balance being hydrogen. The air was supplied by an in house system. The CO blend and air-streams were joined at the inlet to a jacketed glass tube with an outer jacket for circulating coolant. The glass tube was cooled by a temperature controlled circulating bath which
15 could control the temperature to a specific temperature chosen from within a range of 5°C to about 100°C. The catalyst was loaded inside the glass tube.

The catalyst was prepared as set out in Examples I-III. A quantity of 2.0 grams of the treated catalyst was loaded into the glass tube with mesh quartz chips packed into the void space. Each catalyst was pretreated by heating to 97°C for one
20 hour with 100 cc/min of hydrogen flow through the catalyst bed. The tests were run with conditions as shown in the table below. All runs were carried out at ambient pressure, at 10,000 cc feed gas per cc catalyst per hour, GHSV (gas hourly space velocity) using a feed of 1 percent CO in hydrogen. Data were taken every 15 minutes with the 30 minute results recorded as the result of the test run.

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TABLE 1

| Pt/Fe and Pt/Fe(Acid Treated) in the Presence of Hydrogen | | | | | | | | |
|---|-----|---------------|-----------------------|-----------------------|----------------------|----------|--------------------|----------------------------|
| | Cat | React Temp °C | Target O:CO mol ratio | Actual O:CO mol ratio | %Conv O ₂ | %Conv CO | CO Survival (vol%) | %Select to CO ₂ |
| 5 | A | 80 | 1 | 0.8 | 100.1 | 59.3 | 0.4270 | 75.0 |
| | A | 80 | 2 | 1.6 | 99.9 | 94.9 | 0.0519 | 61.1 |
| | A | 80 | 2.5 | 1.9 | 99.8 | 99.9 | 0.0006 | 51.6 |
| | A | 80 | 2.75 | 2.1 | 99.6 | 100.0 | 0.0000 | 47.2 |
| | A | 80 | 3 | 2.3 | 99.4 | 100.0 | 0.0000 | 43.3 |
| | B | 80 | 1 | 0.8 | 100.0 | 59.5 | 0.4290 | 76.6 |
| 10 | B | 80 | 2 | 1.5 | 100.0 | 97.0 | 0.0314 | 62.7 |
| | B | 80 | 2.5 | 1.9 | 100.0 | 100.0 | 0.0000 | 51.7 |
| | B | 80 | 2.75 | 2.1 | 100.0 | 100.0 | 0.0000 | 47.0 |
| | B | 80 | 3 | 2.3 | 99.9 | 100.0 | 0.0000 | 43.1 |
| | A | 25 | 1 | 0.8 | 90.3 | 85.0 | 0.1570 | 119.2 |
| | A | 25 | 1.5 | 1.2 | 87.6 | 96.5 | 0.0359 | 93.1 |
| 15 | A | 25 | 2 | 1.6 | 84.7 | 98.0 | 0.0202 | 74.4 |
| | A | 25 | 3 | 2.3 | 80.5 | 98.9 | 0.0114 | 52.9 |
| | A | 25 | 4 | 3.1 | 78.3 | 99.0 | 0.0093 | 41.1 |
| | B | 25 | 1 | 0.8 | 94.6 | 88.7 | 0.1200 | 120.7 |
| | B | 25 | 1.5 | 1.2 | 91.5 | 98.9 | 0.0116 | 91.4 |
| | B | 25 | 1.75 | 1.4 | 88.3 | 99.1 | 0.0089 | 82.3 |
| 20 | B | 25 | 2 | 1.5 | 85.5 | 99.3 | 0.0072 | 75.1 |
| | B | 25 | 2.5 | 1.9 | 82.6 | 99.6 | 0.0045 | 62.3 |
| | B | 25 | 3 | 2.3 | 77.1 | 99.4 | 0.0057 | 55.6 |
| | | | | | | | | |

25

In the table above cat is catalyst, react temp is reaction temperature, conv is conversion and select is selectivity.

The data show that both Pt/Fe and the Pt/Fe (acid treated) were effective as catalyst in the conversion of CO to CO₂. In oxygen conversion data the acid treated catalyst had a higher activity than the catalyst that was not acid treated.

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This higher activity occurred under all conditions, including the very high space velocities. At 80°C and 10,000 GHSV the acid treated catalyst had slightly higher CO conversion which resulted in less CO survival and a higher selectivity to CO₂. At 25°C and 10,000 GHSV the acid treated catalyst had higher CO conversion than the untreated catalyst resulting in much lower CO survival and higher selectivity to CO₂.

5 Reasonable variations, modifications and adaptations for various conditions and uses can be made within the scope of this disclosure and the appended claims.

CLAIMS

1. A process for the selective oxidation of carbon monoxide to carbon dioxide in a gaseous mixture comprising hydrogen and carbon monoxide, which process comprises:
 - 5 (A) mixing an amount of free oxygen with said gaseous mixture comprising hydrogen and carbon monoxide to provide an oxygen to carbon monoxide mol ratio in the range of about 0.5 to about 8.0 mol O₂/mol CO to form a second gaseous mixture;
 - (B) contacting the second gaseous mixture at a temperature in the range 10 of about 0°C to about 300°C with an acid treated catalyst comprising platinum and iron impregnated on a support material thereby substantially completely converting carbon monoxide in the second gaseous mixture to carbon dioxide.
2. A process according to claim 1, wherein the support material is chosen from the group consisting of alumina, magnesium aluminate and mixtures thereof.
- 15 3. A process according to claim 2, wherein the support material is alumina.
4. A process according to claim 1, wherein the acid treated catalyst is prepared by a process comprising:
 - (1) impregnating the support material with a solution comprising a 20 platinum compound and a solution comprising an iron compound thereby providing an impregnation mixture comprising an impregnated support material, platinum impregnant, iron impregnant and solvent;
 - (2) heating the impregnation mixture at a temperature for a time sufficient to at least partially drive off the solvent providing thereby a dried catalyst 25 mixture;
 - (3) optionally, repeating steps (1) and (2) at least once;
 - (4) heating the dried catalyst mixture in the presence of an oxygen containing gas at oxidizing conditions to provide an oxidized catalyst mixture;
 - (5) heating the oxidized catalyst mixture in the presence of a reducing atmosphere at reducing conditions to provide a reduced catalyst mixture
 - 30 (6) contacting the reduced catalyst mixture with an acid to provide an

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acid treated catalyst mixture and

(7) contacting the acid treated catalyst mixture with an atmosphere containing free oxygen at a temperature for a time sufficient to provide an oxidized, acid treated catalyst mixture.

5 5. A process according to claim 4, wherein the oxidized catalyst mixture is contacted with an atmosphere containing hydrogen at a temperature for a time sufficient to provide a reduced, oxidized catalyst mixture.

6. A process according to claim 5, wherein the support material is chosen from the group consisting of alumina, magnesium aluminate and mixtures thereof.

10 7. A process according to claim 6, wherein the support material is alumina.

8. A process according to claim 5, wherein the temperature at which the impregnated mixture is heated is in a range of about 125°C to about 225°C and the time at which the impregnated mixture is heated is in a range of about 0.5 hr. to about

15 1.5 hr.

9. A process according to claim 8, wherein the temperature at which the dried catalyst mixture is contacted with an atmosphere containing free oxygen is in a range of about 100°C to about 600°C and the time at which the impregnated mixture is heated is in a range of about 0.5 hr. to about 1.5 hr.

20 10. A process according to claim 4, wherein the acid used in the acid treatment is nitric acid.

11. A process according to claim 5, wherein the temperature at which the oxidized catalyst mixture is contacted with an atmosphere containing hydrogen is in the range of about 200°C to about 400°C and the time at which the oxidized catalyst mixture is contacted with an atmosphere containing hydrogen is in the range of about 2 hr. to about 4 hr.

12. A process for the selective oxidation of carbon monoxide to carbon dioxide in a gaseous mixture comprising hydrogen and carbon monoxide, which process comprises:

30 (A) mixing an amount of free oxygen with said gaseous mixture comprising hydrogen and carbon monoxide to provide an oxygen to carbon monoxide

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mol ratio in the range of 0.5 to about 8.0 mol O₂/mol CO to form a second gaseous mixture;

(B) contacting the second gaseous mixture at a temperature in the range of about 0°C to about 300°C with a catalyst comprising platinum and iron

5 impregnated on a support material thereby substantially completely converting the carbon monoxide in the second gaseous mixture to carbon dioxide wherein the catalyst is prepared by a process comprising:

(1) impregnating the support material with a solution comprising a platinum compound and a solution comprising an iron compound thereby providing an 10 impregnation mixture comprising an impregnated support material, platinum impregnant, iron impregnant and solvent;

(2) heating the impregnation mixture at a temperature for a time sufficient to at least partially drive off the solvent providing thereby a dried catalyst mixture;

15 (3) optionally, repeating steps (1) and (2) at least once and

(4) heating the dried catalyst mixture in the presence of an oxygen containing gas at oxidizing conditions to provide an oxidized catalyst mixture;

(5) heating the oxidized catalyst mixture in the presence of a reducing atmosphere at reducing conditions to provide a reduced catalyst mixture

20 (6) contacting the reduced catalyst mixture with an acid to provide an acid treated catalyst mixture and

(7) contacting the acid treated catalyst mixture with an atmosphere containing free oxygen at a temperature for a time sufficient to provide an oxidized, acid treated catalyst mixture.

25 13. A process for the selective oxidation of carbon monoxide to carbon dioxide in a gaseous mixture comprising hydrogen and carbon monoxide, which process comprises:

(A) mixing an amount of free oxygen with said gaseous mixture comprising hydrogen and carbon monoxide to provide an oxygen to carbon monoxide 30 mol ratio in the range of 0.5 to about 8.0 mol O₂/mol CO to form a second gaseous mixture;

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- (B) contacting the second gaseous mixture at a temperature in the range of about 0°C to about 300°C with a catalyst comprising platinum and iron impregnated on a support material thereby substantially completely converting the carbon monoxide in the second gaseous mixture to carbon dioxide wherein the catalyst is prepared by a process comprising:
- 5 (1) impregnating the support material with a solution comprising a platinum compound and a solution comprising an iron compound thereby providing an impregnation mixture comprising an impregnated support material, platinum impregnant, iron impregnant and solvent;
- 10 (2) heating the impregnation mixture at a temperature for a time sufficient to at least partially drive off the solvent providing thereby a dried catalyst mixture;
- 15 (3) optionally, repeating steps (1) and (2) at least once and
 (4) heating the dried catalyst mixture in the presence of an oxygen containing gas at oxidizing conditions to provide an oxidized catalyst mixture;
- 20 (5) heating the oxidized catalyst mixture in the presence of a reducing atmosphere at reducing conditions to provide a reduced catalyst mixture;
 (6) contacting the reduced catalyst mixture with an acid to provide an acid treated catalyst mixture;
- 25 (7) contacting the acid treated catalyst mixture with an atmosphere containing free oxygen at a temperature for a time sufficient to provide an oxidized, acid treated catalyst mixture and
 (8) contacting the oxidized, acid treated catalyst mixture with an atmosphere containing hydrogen at a temperature for a time sufficient to provide a reduced, oxidized, acid treated catalyst mixture.

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US00/42050

A. CLASSIFICATION OF SUBJECT MATTER

IPC(7) : C01B 31/20
US CL : 423/437.2, 213.5, 247; 502/339

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
U.S. : 423/437.2, 213.5, 247; 502/339

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

| Category * | Citation of document, with indication, where appropriate, of the relevant passages | Relevant to claim No. |
|------------|--|-----------------------|
| X | US 5,017,357 A (KOLTS et al.) 21 May 1991 (21.05.1991) | 1-13 |

Further documents are listed in the continuation of Box C.

See patent family annex.

* Special categories of cited documents:

- | | |
|--|--|
| <ul style="list-style-type: none"> "A" document defining the general state of the art which is not considered to be of particular relevance "E" earlier application or patent published on or after the international filing date "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) "O" document referring to an oral disclosure, use, exhibition or other means "P" document published prior to the international filing date but later than the priority date claimed | <ul style="list-style-type: none"> "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art "&" document member of the same patent family |
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Date of the actual completion of the international search

13 March 2001 (13.03.2001)

Date of mailing of the international search report

11 APR 2001

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